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Temporal variability of atmospheric particulate matter and chemical composition during a growing season at an agricultural site in northeastern China

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ABSTRACT

This study presents the observations of PM_{10} and $PM_{2.5}$ concentrations at an agricultural site from April to October 2012 in Dehui city, China. Ambient air was sampled by filter-based samplers and online PM monitors. The filter samples were analyzed to determine the abundance of ionic/inorganic elements, organic carbon (OC) and elemental carbon (EC). The daily PM_{10} concentrations varied significantly over the monitoring period, with an average of 168 ± 63 (in the range of 52–277) $\mu g/m^3$ during the land preparation/planting period (26 April–15 June), 85 ± 65 (36–228) $\mu g/m^3$ during the growing season (16 June–25 September), and 207 ± 88 (103–310) $\mu g/m^3$ during the harvest period (26 September–31 October). $PM_{2.5}$ accounted for 44%, 56% and 66% of atmospheric PM_{10} during these periods, respectively. The PM_{10} diurnal variation showed a distinct peak from 16:00 to 21:00 (LST) during the growing and harvesting seasons, while a gradual increase throughout the daytime until 17:00 was observed during tilling season. Mineral dust elements (Al, Ca, Fe, and Mg) dominated the PM_{10} chemical composition during the tilling season; OC, NO_3^-, SO_4^{2-} and NH_4^+ during the growing season; and carbonaceous species (*i.e.*, OC and EC) during the harvesting season. Our results indicate that the soil particles emitted by farm tillage and organic matter released from straw burning are the two most significant sources of PM_{10} emissions contributing to the recurring high pollution events in this region. Therefore, development of agricultural PM inventories from soil tillage and straw burning is prioritized to support air quality modeling.

Introduction

Over the last decades, the frequency of regional atmospheric haze events has rapidly increased in China (Kan et al., 2012). As one of the primary atmospheric pollutants, the issue of particulate matter (PM) emission has gradually grown in importance (Zhang et al., 2012). In agriculture-dominated regions, farming activities can significantly affect local air quality or contribute to regional haze events, especially in arid and semiarid regions with intense field activities (Hinz and Tamoschat-Depolt, 2007). However, studies have shown large temporal–spatial differences in agricultural PM emissions because of the various field

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operations, crop types, soil properties and climate conditions (Carvacho et al., 2004; Funk et al., 2008; Holmén et al., 2008; Aneja et al., 2009; Aimar et al., 2012).

Agricultural activities emit considerable primary PM and gaseous precursors (*e.g.*, ammonia, VOC and chemical substances) of secondary PM (Hinz and Tamoschat-Depolt, 2007). Soil tillage, crop harvesting and straw burning have been identified as the three largest anthropogenic sources of agricultural PM emission. Nordstrom and Hotta (2004) have noted that aeolian transport of cultivated and grazed soil is a global problem, and the disturbance of soil and plants could increase the frequency of dust events. Previous studies have indicated that the magnitude of the mechanically generated PM emission might be several times that of wind erosion of cropland, although these activities only occurred over a few days or weeks (Goossens et al., 2001). Agricultural burning releases a significant number of airborne fine particles that can rapidly spread, thus receiving more attention (Zhang et al., 2007). In many agricultural regions, spring plowing, fall harvesting and straw burning are responsible for regional haze events (Zhang et al., 2010; Qin and Xie, 2011).

Northeastern China is a major region for crop production and covers approximately 20% of the total arable land area in China (National Bureau of Statistics of China, 2011). Bare soils in the region are exposed to the atmosphere for up to seven months because the single cropping pattern is dominant. Natural wind erosion and agricultural disturbance could increase the potential of PM emissions from the soil (Nordstrom and Hotta, 2004) and decrease the soil organic matter content (Harper et al., 2010). Additionally, most straw residues are openly burned to start the farming season and to reduce the cost of recycling in this region. However, the information about rural air quality and the mechanism, magnitude, and patterns of agricultural emission sources of PM is scarce (*e.g.*, Han et al., 2010; Huang et al., 2011). As air quality concerns become increasingly prominent in northeastern China, the lack of information may impede air quality modeling and control measures in agricultural activities.

This study presents our results on rural air quality and estimated farm activity roles on PM emissions in a maize-dominant area of northeastern China. Using portable filter-based samplers and real-time monitors, we measured the atmospheric concentrations of PM_{10} and $PM_{2.5}$ at a farmland site near Changchun City from the end of April to the end of October 2012. The major chemical components of the sampled PM_{10} filters were also analyzed in the laboratory. Our primary obective was to understand the relationships among the characteristics of the PM concentration levels, their chemical compositions and the field farming activities in northeastern China.

1. Materials and methods

1.1. Sampling site

The sampling site was located at a farmland in the black-soil protection agro-technical station (ATS, 44°12′29″N, 125°34′04″E). This farm station is on the edge of a village and is approximately 50 km away from the center of Changchun City, the capital of Jilin Province, China. Note that this station is adjacent (~30 m) to a local small chicken house with length of 20 m and width of 10 m, and chicken manure consistently accumulates in the ditch close to the station. The National Road 102 is approximately 300 m away from the station. The local climate is characterized as a semi-humid temperate continental monsoon climate (Chen et al., 2015). The long-term (30 year) mean annual temperature is 4.4°C, with a mean January temperature of –15.1°C and a July mean of 23.1°C. The annual precipitation is 522–615 mm, of which more than 70% falls in the summer from June to August. The soil type at the investigated site is clay loam soil (*Typic hapludoll*), with a mean organic carbon content of 1.65%, a mean pH of 6.48, and a mean bulk density of 1.24 g/cm^3 at the depth of 0.05 m. Maize is the dominant upland crop, accounting for 53% of the total arable land in Jilin Province (Bureau of Statistic of Jilin Province, 2012). In this region, spring tillage begins at the end of April and ends in mid-June, the vegetation period is from June to September, and crops or straw are harvested or burned in October.

1.2. Atmospheric PM sampling

The sampling period lasted for six months from the end of April to the end of October 2012. The sampling heights were approximately 3 m (*i.e.*, top of the support frame of the sampler) at the ATS site. Using a filter-based gravimetric sampling method, the atmospheric PM_{10} and $PM_{2.5}$ were sampled every one or two days during tillage and harvest periods and twice a month during the vegetation period. Portable samplers (Model Omni, BGI Inc., USA) were used with a flow-rate of 5 L/min on a 24-hr basis. Two types of 47 mm Teflon and Quartz filters (Whatman PTFE and QM-A, General Electric Co., Maidstone, UK) were applied to collect atmospheric particles. The mass concentrations of PM were calculated by division of the weight increase in the filter and the standard sampling air volume, which was converted using the actual air volumes and, periodically, the air temperature and pressure. These filters were weighed on an electronic microbalance with a precision of 0.01 mg (Model XS105DU, Mettler Toledo Inc., Zurich, Switzerland). Before and after filter sampling, the filters were stored in a dessicator at 20–25°C and 35%–45% relative humidity for 48 hr. Subsequently, the sampled filters were stored in a refrigerator at 4°C until chemical component analysis.

Meteorological data, including the daily precipitation, air temperature, relative humidity, visibility, wind speed and direction, were obtained from the Changchun Meteorological Bureau.

1.3. Chemical component analysis of PM_{10}

Teflon PM_{10} filters were used to measure the ionic speciation, including anions (*i.e.*, F^-, Cl^-, NO_3^- and SO_4^{2-}), cations (Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}), and inorganic elements (*i.e.*, Al, Ca, Fe, Mg, K, Mn, Ni, Cu, Zn, As, Se, Sr, Ba, Cd, Cr, Nd, and Pb). The concentrations of anions and cations were determined by ion chromatography (ICS-1000, Dionex Inc., Sunnyvale, CA, USA). The eluent used for the anions was a 3.5 mmol Na_2CO_3/1.0-mmol $NaHCO_3$ solution, whereas a 20 mmol methane sulfonic acid (MSA) solution was used as the cation eluent. The ion chromatography method had a detection limit of 0.05 mg/L and an uncertainty of ±10% for all of the ions. For the inorganic elements, the Teflon filter was extracted for 0.5 hr using 6 mL HNO_3 and 2 mL HCl in a microwave laboratory system with a power of 1400 W, 170°C as

the maximal temperature and an ultimate pressure of 20 bar before the determination. The extracted solution was injected into an inductively coupled plasma-atomic emission spectrometer (ICP-AESIRIS Intrepid II, Thermo Electron Corp., Beverly, MA, USA) to obtain the element concentrations. The precision and bias of the element concentrations of the ICP-AESIRIS method were typically less than 10%. The concentration of mineral dust was calculated by summing the content of the oxides of Al, Si, Ca, Fe, Mg and K, (*i.e.*, 1.89 Al + 2.14 Si + 1.40 Ca + 1.43 Fe + 1.66 Mg + 1.21 K) (Hueglin et al., 2005). The Si concentration was estimated according to the average ratio of Si/Al (3.6) in the earth's crust (Hueglin et al., 2005) because Si was not determined by the ICP-AESIRIS method in this study.

Quartz filters were used to determine the particulate EC and OC concentrations using a thermal-optical carbon aerosol analyzer (Sunset-OCEC RT-4, Sunset Lab Inc., Tigard, OR, USA) (Aneja et al., 2006). This method is based on the thermal desorption/oxidation of particulate carbon to CO_2, which is then reduced to methane and, subsequently, measured using a flame-ionization detector. The analysis sequence was initialized in a nonoxidizing atmosphere (helium) with a 10 sec purge followed by four temperature ramps to a maximum of 900°C. A cooling blower was then used to decrease the temperature to 600°C before oxygen was added. The temperature was maintained at this point until the transmittance or reflectance returned to the initial value before the sample was heated. This point determines the distinction between the OC and EC, *i.e.*, all of the carbon measured up to this point is OC, whereas all of the carbon measured after this point is EC. The total carbon in this study refers to the sum of EC and OC. The precision is 0.19 at 1 μg of carbon and 0.01 at 10–72 μg of carbon.

1.4. Diurnal variation of the PM_{10} measurement

During each period, *i.e.* tillage period (TP), vegetation period (VP) and harvest period (HP), three or four sunny days were selected to measure the diurnal PM_{10} concentrations using a real-time DUSTTRAK™ Aerosol Monitor (Model 8520, TSI Inc., Shoreview, MN, USA). The monitor is based on light scattering technology and was regulated to record data at a frequency of 1 min (Yanosky et al., 2002).

An aerosol sample is drawn into the sensing chamber in a continuous stream, and particles in the aerosol stream scatter light in all directions. A laser beam collects a portion of the scattered light and focuses it onto a photodetector. The detection circuitry converts the light into a voltage; this voltage is proportional to the amount of light scattered, which is proportional to the mass concentration of the aerosol. The

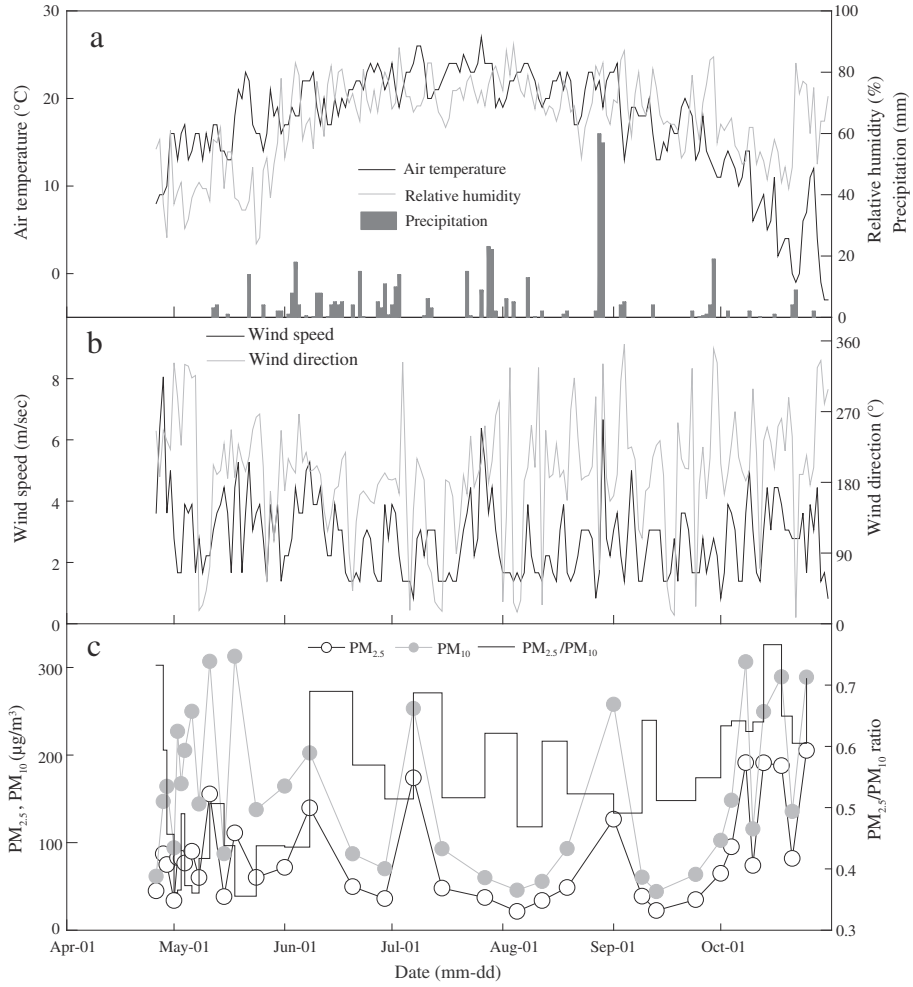

Fig. 1 – Temporal variations in (a) air temperature, relative humidity, precipitation, (b) wind speed, wind direction, and (c) PM_{10} and $PM_{2.5}$ mass concentrations and their ratio at the investigated rural site in 2012.

portability and low-power-supply requirement of this monitor ensures that the PM determination could be performed simultaneously at four sites, which is especially useful at rural sites without good infrastructure.

1.5. Data analysis

Pearson correlations were obtained between the PM and the components and among the components. The significance of the differences in the PM concentrations and the chemical components were investigated using the independent-samples t test. All of the statistical procedures were performed using the software SigmaPlot 10.0 (SPSS Inc., Chicago, IL, USA).

2. Results

2.1. Meteorological factors and farming activities

The mean air temperature (17.4°C), relative humidity (65%) and wind speed (2.7 m/sec) from May to October 2012 were comparable to the ten-year average values for the same period from 2004 to 2013 (Fig. 1a and b). The total precipitation (453 mm) was higher than the long-term mean (405 mm), indicating a slightly wet year.

Farming activities, including soil tillage, crop harvesting and straw burning, are related to precipitation. Most of the soil tillage and crop plant operations were conducted before May 11 because of the fifteen continuous sunny days that occurred before that date. Frequent rain occurred throughout the vegetation period (June to September), and an extreme rain event (107 mm) occurred from 28 to 29 August. In October, rainfall occurred every three or four days, although the sum of the precipitation was similar to the average.

2.2. Temporality of atmospheric PM

(1) Seasonal pattern: The daily concentrations of PM_{10} and $PM_{2.5}$ at the farm site ranged from 44 to 313 $\mu g/m^3$ and from 21 to 205 $\mu g/m^3$ during the sampling period, respectively (Fig. 1c). The temporal coefficients of variation (CV) were 55% for PM_{10} and 63% for $PM_{2.5}$. The ratios of $PM_{2.5}$ to PM_{10} varied from 36% to 77% during the investigated period and averaged 44% ± 9%, 55% ± 7% and 66% ± 2% at TP, VP and HP, respectively. Compared with VP (85 ± 65 $\mu g/m^3$), significantly higher PM concentrations occurred, with an average of 168 ± 63 and 207 ± 88 $\mu g/m^3$, respectively (Table 1). Although low average PM concentrations were determined during VP, two high values, *i.e.* 253 and 258 $\mu g/m^3$, were observed on 7 July and 1 September.

(2) Diurnal pattern: The diurnal variations of the PM_{10} percent concentration at the farm site were different during TP, VP and HP (Fig. 2). During the soil tillage, the PM_{10} concentrations had a unimodal pattern, with a gradual increase in the daytime, and reached the highest values at 16:00–18:00 local time. The vegetation period had a typical bimodal pattern of PM_{10} variations, and two peaks appeared at 7:00 and 18:00–`19:00. The PM_{10} levels at other times were significantly lower than these two times during VP. Similar to VP, the PM_{10} pattern during HP showed that the PM_{10} concentrations were low from 10:00–18:00, increased rapidly to a peak from 20:00 to 22:00 and then gradually decreased. There was another minor peak in the PM_{10} concentrations at approximately 7:00.

2.3. Chemical composition of atmospheric PM_{10}

Fig. 3 presents the temporal variations of the four types of components, *i.e.* secondary aerosol-related ions, mineral dust-related elements, carbonaceous species and K^+. The ranges of the NO_3^-, SO_4^{2-} and NH_4^+ concentrations were 0–13, 1–25 and 1–34 $\mu g/m^3$, respectively (Fig. 3a). The peaks of these three ion peaks were consistent with the highest PM concentrations during the vegetation period. Mineral dust-related elements had a similar temporal trend, with the highest values of 11 $\mu g/m^3$ Al, 10 $\mu g/m^3$ Ca, 4 $\mu g/m^3$ Fe, and 2 $\mu g/m^3$ Mg observed at soil

Table 1 – Atmospheric PM_{10} and $PM_{2.5}$ mass concentrations and major chemical components of PM_{10} at the investigated rural site during the tillage period (26 April–15 June), vegetation period (16 June–25 September) and harvest period (26 September–31 October) in 2012.

Component	Tillage ($\mu g/m^3$)	Vegetation ($\mu g/m^3$)	Harvest ($\mu g/m^3$)	Overall ($\mu g/m^3$)
PM_{10}	168 ± 63.4 (51.8–276.9)	85 ± 65.1 (36.4–228.4)	207.3 ± 87.8 (103.8–310.6)	148.5 ± 83.8 (36.4–310.6)
$PM_{2.5}$	83.5 ± 36.8 (34.0–155.6)	56.0 ± 46.1 (21.4–174.0)	136.5 ± 62.1 (65.0–205.4)	86.5 ± 55.8 (21.4–205.4)
NH_4^+	2.6 ± 2.2 (0.3–8.2)	3.1 ± 3.8 (0.4–12.7)	4.2 ± 3 (0.7–9.2)	3.1 ± 3 (0.3–12.7)
Ca^{2+}	1.5 ± 0.6 (0.8–2.9)	1.1 ± 0.4 (0.7–1.9)	1.7 ± 0.6 (1.2–3)	1.4 ± 0.6 (0.7–3)
K^+	0.8 ± 0.4 (0.4–1.7)	0.7 ± 0.3 (0.3–1.4)	2.1 ± 1 (1.1–4.2)	1.1 ± 0.8 (0.3–4.2)
Na^+	0.4 ± 0.2 (0.1–1.7)	0.3 ± 0.2 (0.1–0.7)	0.6 ± 0.6 (0.3–2)	0.4 ± 0.3 (0.1–2)
SO_4^{2-}	5.8 ± 5.1 (0.8–16.9)	8.8 ± 11.1 (1.9–33.6)	5.8 ± 3.3 (2.2–11.7)	6.8 ± 7.4 (0.8–33.6)
NO_3^-	4.8 ± 3.8 (1.1–15.4)	4.5 ± 6.5 (1.2–24.6)	8.5 ± 5.9 (2.5–19.1)	5.6 ± 5.4 (1.1–24.6)
Cl^-	1.5 ± 1 (0.3–3.8)	1.2 ± 1.1 (0.2–4)	5.5 ± 5.1 (1.7–17)	2.3 ± 3 (0.2–17)
Mineral	71.8 ± 34.3 (4.3–132.3)	5.4 ± 6.8 (2.1–26.6)	18 ± 11.1 (4.8–35.5)	36.8 ± 38.7 (2.1–132.3)
TE	1.2 ± 0.6 (0–2.4)	0.4 ± 0.5 (0–1.3)	1.1 ± 0.7 (0.3–2.5)	0.9 ± 0.7 (0–2.5)
OC	34.9 ± 12.2 (18–58)	29.6 ± 22.9 (12.7–84.7)	102.5 ± 50.1 (47–162.7)	48.5 ± 40.5 (12.7–162.7)
EC	6.1 ± 2.5 (2.6–12)	5.2 ± 4.7 (2–15)	11.2 ± 5 (6–18)	6.9 ± 4.5 (2–18)

The figures outside of the parentheses are the daily means during the entire sampling period and the standard deviation, and those inside of the parentheses are their ranges. Mineral, TE, OC and EC refers to the mineral dust, trace elements, organic carbon and elemental carbon in the atmospheric PM_{10} samples.

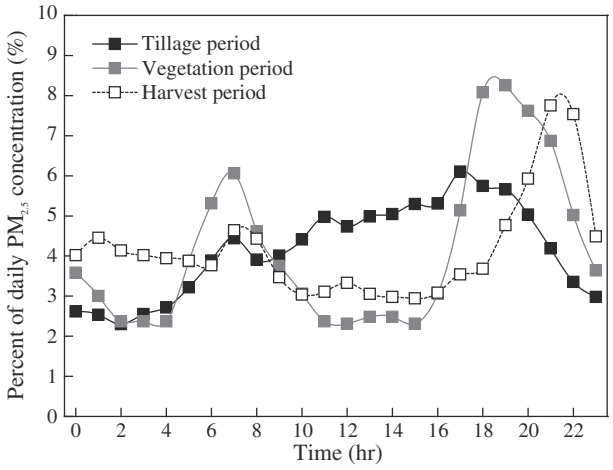

Fig. 2 – Diurnal variations of airborne PM_{10} percent concentrations during the crop tillage period in May, the vegetation period from mid-June to mid-September and the harvest period in October at the farm site.

tilling and planting before mid-June (Fig. 3b). For carbonaceous species, the OC concentrations significantly varied from 13 to 163 μg/m^3, and the EC varied over the range of 2–18 μg/m^3. There were significantly higher OC levels during the harvest period, and two high values appeared during the vegetation period (Fig. 3c). The maximum of K^+ (4 μg/m^3) was observed in October followed by May and June.

Table 1 and Fig. 4 summarize the averages of the major chemical components and their ratios during the three periods. During TP, mineral dust (72 ± 34 μg/m^3) and OC (35 ± 12 μg/m^3) were the primary contributors, accounting for 41% and 24% of the sampled PM_{10}, respectively. The vegetation period significantly reduced the mineral dust components (5 ± 7 μg/m^3), maintained a similar level of OC, and slightly increased the secondary aerosol-related ions. The contributions of the carbonaceous species (OC + EC) and the secondary aerosol ions (NO_3^-, SO_4^{2-} and NH_4^+) to PM_{10} were 41% and 16%, respectively. During HP, the carbonaceous species averaged 112 ± 55 μg/m^3, which was the dominant PM_{10} (53%) followed by mineral dust (10%) and secondary aerosol ions (8%).

3. Discussion

This study provides a preliminary insight into the temporal trends, pollution levels, and chemical composition of rural PM in northeastern China. This information also aids in the identification of the PM emission sources and their characteristics (*e.g.*, chemical and diurnal profiles) in the typical agricultural region.

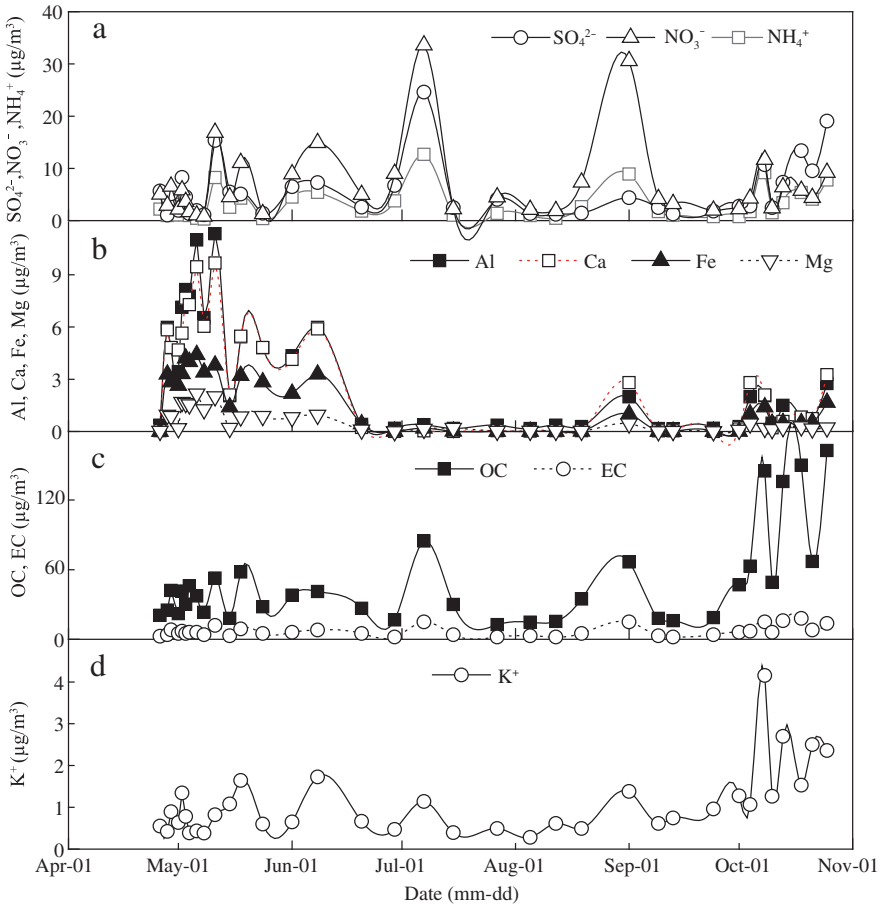

Fig. 3 – Temporal variations in (a) secondary aerosol-related ions (NH_4^+, NO_3^- and SO_4^{2-}), (b) dust-related elements (Al, Ca, Fe and Mg), (c) carbonaceous species (OC and EC) and (d) biomass burning marker (K^+) at the investigated rural site in 2012. OC: organic carbon; EC: elemental carbon.

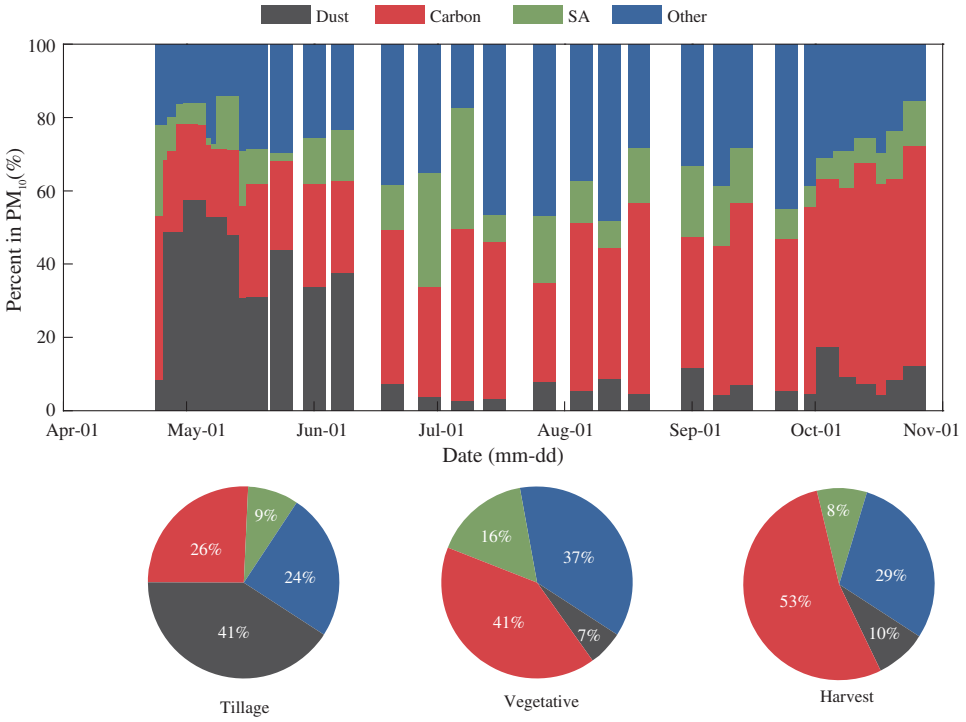

Fig. 4 – Temporal variations of the individual contributions of dust (dust), carbonaceous species (carbon), secondary aerosol (SA) and other to the atmospheric PM_{10} at the rural site and the corresponding average of the four compositions during the tillage period (26 April–15 June), vegetative period (16 June–25 September) and harvest period (26 September–31 October) in 2012. Secondary aerosols (SAs) include ammonium, nitrate and sulfate. Mineral dust (dust) was calculated from the oxide content of Al, Si, Ca, Fe, Mg and K. Carbonaceous species (carbon) represent the sum of organic carbon (OC) and elemental carbon (EC).

These levels of daily PM_{10} (44–313 μg/m^3) or $PM_{2.5}$ concentrations (21–205 μg/m^3) fall in the range of reported values at the Tongyu rural site (Spring $PM_{2.5}$: 23–1630 μg/m^3) (Zhang et al., 2008) and are comparable with those at the Longfengshan rural site (Annual PM_{10}: 82 μg/m^3) (Zhang et al., 2012) in northeastern China. The 24-hr mean of the PM_{10} and $PM_{2.5}$ concentrations provided by the secondary standard of the National Ambient Air Quality Standard in China (NAAQS) is 150 and 75 μg/m^3, respectively (Ministry of Environmental Protection of People's Republic of China, 2012). Judging by the NAAQS standards of China, the maximum PM_{10} and $PM_{2.5}$ concentrations were double and triple the standard levels, respectively. During the soil tillage and crop harvest periods, approximately 60% of the samples exceeded the standard, while 80% of the PM values met the standard during the crop growing season. The rural PM concentrations were generally dependent on the local background level, and the increased portions came primarily from the periodic agriculture-induced PM releases. Conventional field tilling practices, *e.g.* plowing, disking, listing, compacting and planting, can generate minerals (soil origin) or a combination of mineral and organic dust (plant origin) due to bare soil disturbance (Bogman et al., 2005). These emission sources represented the most significant contribution of mineral elements (41%) of airborne PM_{10} samples, and the $PM_{2.5}/PM_{10}$ ratios (40%) were low during soil tillage (Figs. 1c and 4). Moreover, recurring dust from farm vehicles moving on unpaved or paved roads in the surrounding area may be significant in the fugitive PM_{10} concentrations. The second highest contribution to the PM levels came from OC and EC during this period (Fig. 4), which were most likely from fuel consumption due to the increased usage of agricultural machinery, and spring straw burning or roadside garbage burning based on the detected K^+ (Fig. 3d). Continuously high Fe levels in the soil tillage period compared with the other periods (Fig. 3b) were mostly attributed to the soil/mineral dust, as Fe is one of the common crustal elements. In addition, the increase of agricultural vehicles or machines during soil tillage could enhance Fe emission because the coarse particle mode of Fe may be emitted or formed in the aging process by vehicles using gasoline and diesel fuel (Fang et al., 2003).

During the vegetation period, the PM concentrations significantly decreased, and the ratio of fine particles in PM_{10} obviously increased. The mineral dust emissions can be ignored with the end of field activities and the increase in the soil coverage by crop growth and rainfall. Frequent rainfall events significantly improve the air quality by removing the air particles by wet deposition. Two high PM events were observed on 7 July and 1 September, which presented a high loading of NO_3^-, SO_4^{2-}, and NH_4^+ along with OC. These ions represent the basic characteristics of nitrate and sulfate, which are formed during photochemical reaction-induced secondary pollution (Cao et al., 2005). The July 7 episode was on the third day after a 10-day moderate rain period, and the mean wind speed was 3 m/sec, indicating a calm air flow condition. The weather on this day was suitable for farm weeding and foliage spraying, and most activities were

conducted by farm machines. On the one hand, agricultural activities in the field and vehicular emissions from National Road 102 could directly contribute to PM emissions by farm machinery and soil/crop disturbance; on the other hand, PM emissions from industrial or transportation sources that generated gas precursors for secondary aerosols were accumulated in weather conditions unfavorable to air diffusion. In addition, high ammonium concentrations most likely arose from chicken manure fermentation, because the manure consistently accumulated around the observation station. Therefore, both enhanced emission sources and unfavorable diffusion conditions were the contributors to this high PM event. For the second event, there were no corresponding agricultural activities in this period. The high contents of NO_3^- and OC may have resulted from the regional photochemical smog. On the observation day, the visibility (7 km) from the Changchun Weather Bureau was significantly lower than on the other sunny day (11–16 km).

Field operations during the crop harvest include reaping maize, straw burning, transporting maize stalks to homes for fuel during the winter, and fall plowing. These activities were directly affected by rainfall events. In October, we did not observe a large-scale straw burning phenomenon because the crop straw was not sufficiently dry for burning under the conditions of short intervals between rainfalls (three or four days). During the crop harvest, the PM samples over four days were above the Chinese standard. During these days, the PM_{10} concentrations were comparable to those in the soil tillage period, while the $PM_{2.5}$ concentrations were significantly higher than those in the other periods (Fig. 1c). Carbonaceous species dominated the principal components of airborne PM_{10}, with a contribution of ~50%. Even the burning events were not strong in the observed period, which could elevate the OC contents. Furthermore, as the tracer of biomass burning, the increase of K^+ and K confirmed its emission in agricultural burning operations. Previous studies have reported that particles from biogenic burning would become finer with age, and a high content of NO_3^- and SO_4^{2-} was found in aged particles (Hays et al., 2005; Zhang et al., 2007). Similarly, increasing the NO_3^- and SO_4^{2-} concentrations at the post-harvest stage also supported the importance of biomass burning to secondary aerosol formation. The mineral dust-related element concentrations in this harvest season were significantly lower than that during soil tilling, although agricultural machines and vehicles were also used in the field. The weak mineral dust emissions should be ascribed to the limited fugitive dust under the wet topsoil condition and the reduction in the use of the harvesting machinery due to frequent rainfall events.

Local chemical and temporal profiles induced by agricultural operations are of significant importance in air quality models, providing the key parameters (Hinz and Tamoschat-Depolt, 2007). In this study, the particle chemical profile of the field operations was not directly determined under controlled conditions. We indirectly estimated the chemical profile induced by soil tillage and crop straw burning by calculating the increased PM_{10} concentrations and components on the obviously polluted days with field operations and without field operations, *i.e.*, pre-tilling before 1 May or pre-harvest days from September to October. Based on the field tilling-induced chemical profile of PM_{10} (Fig. 5), the operation raised the mineral-related elements by more than 53% (*i.e.*, Si, Al, Ca, Mg, and Fe) by disturbance of the soil, and released considerable OC (~21%) through fuel consumption by diesel machinery. The straw burning primarily produced OC (~56%) and EC (~5%), while secondary aerosol-related NO_3^-, SO_4^{2-} and NH_4^- were formed in the aging process.

We assumed that the PM_{10} concentrations in the vegetation period represented the background (except for 4 July and 1 September). The differences in the hourly PM_{10} concentrations between the tillage period/harvest period and the background values were calculated as tilling- and burning-induced emissions. Because the high concentrations generally depend on the emission strength and the planetary boundary layer (PBL) height, we adjusted the diurnal profiles using PBL heights simulated from the Weather Research and Forecasting model (Fig. 6). According to these results, field tilling operations strongly emitted PM_{10} from 10:00 to 17:00, while the PM_{10} release from crop burning primarily occurred from 14:00 to 18:00. The estimated diurnal profiles from the field activities appear coincident with the local conventional practice, according to the farmers.

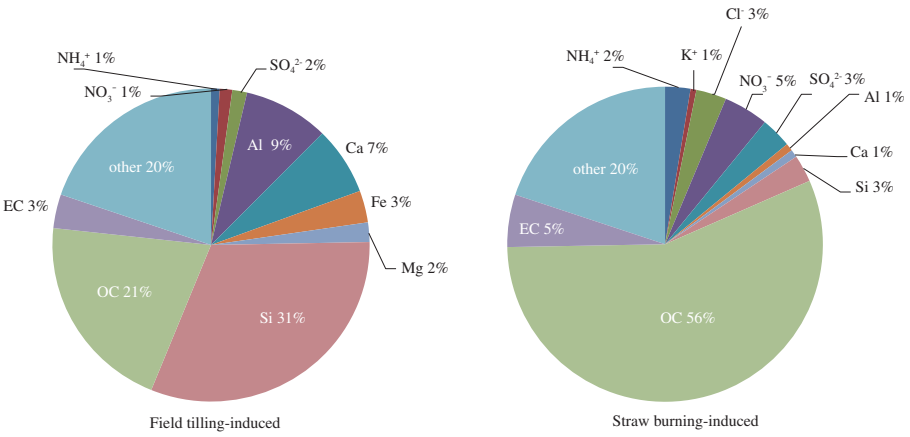

Fig. 5 – Estimated chemical profiles of field tilling-induced and straw burning-induced PM_{10} emission.

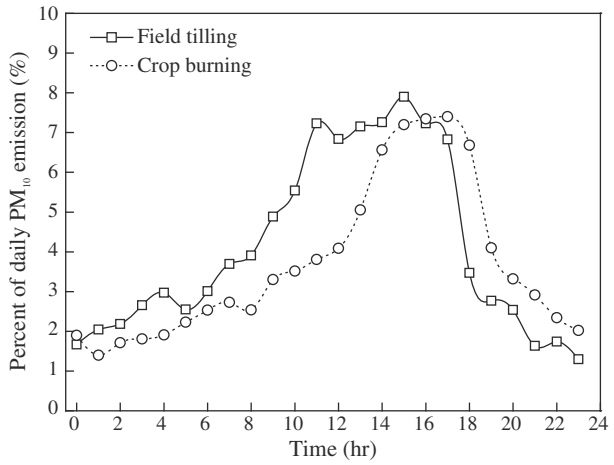

Fig. 6 – Diurnal profile of planetary boundary layer (PBL)-adjusted field tilling- and crop burning-induced PM_{10} emission.

Our *in-situ* investigations confirm that soil tilling in May and crop burning in October are the most significant regional sources for particulate matter emission in the maize-dominant area in northeastern China. Creating an inventory of agricultural PM emission will improve the accuracy of load forecasting in local or even regional air quality. However, estimated parameter patterns concerning the chemical and diurnal profiles of these operations require further research because we were unable to provide sufficient replicates of the agricultural regions and the temporal coverage of PM_{10} (*i.e.*, real-time observation) to precisely account for the diurnal variations resulting from infrastructural constraints.

4. Conclusions

Farmland tillage and crop straw burning from a maize-dominated region in northeastern China were identified as the most significant agricultural operations for area sources of PM emissions. Mineral dust and OC were the primary chemical compositions during the tillage period, while straw burning generated substantial OC during the harvest period. The short interval between rainfall events in May and October may significantly reduce the PM emissions by regulating the agricultural operations and increasing the soil moisture. The estimated diurnal profile of the PM_{10} emissions showed that soil tillage and planting practices were conducted nearly the entire day, while crop straw appeared to be burned mostly in the afternoon. The chemical and diurnal profiles of PM emission from field tilling and straw burning are useful to model local or regional air quality. In addition, our study revealed PM_{10} and $PM_{2.5}$ events that were two times the level from these activities, indicating that other agricultural practices in the countryside, such as animal production or unconventional activities, are also potential sources of PM emission. However, the observation frequency of the PM concentrations and the chemical component analysis were insufficient to further identify these sources.

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